

**ESCA STUDIES OF METALS
AND OXIDES**

Gunnar Schön

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General Section



June 1973

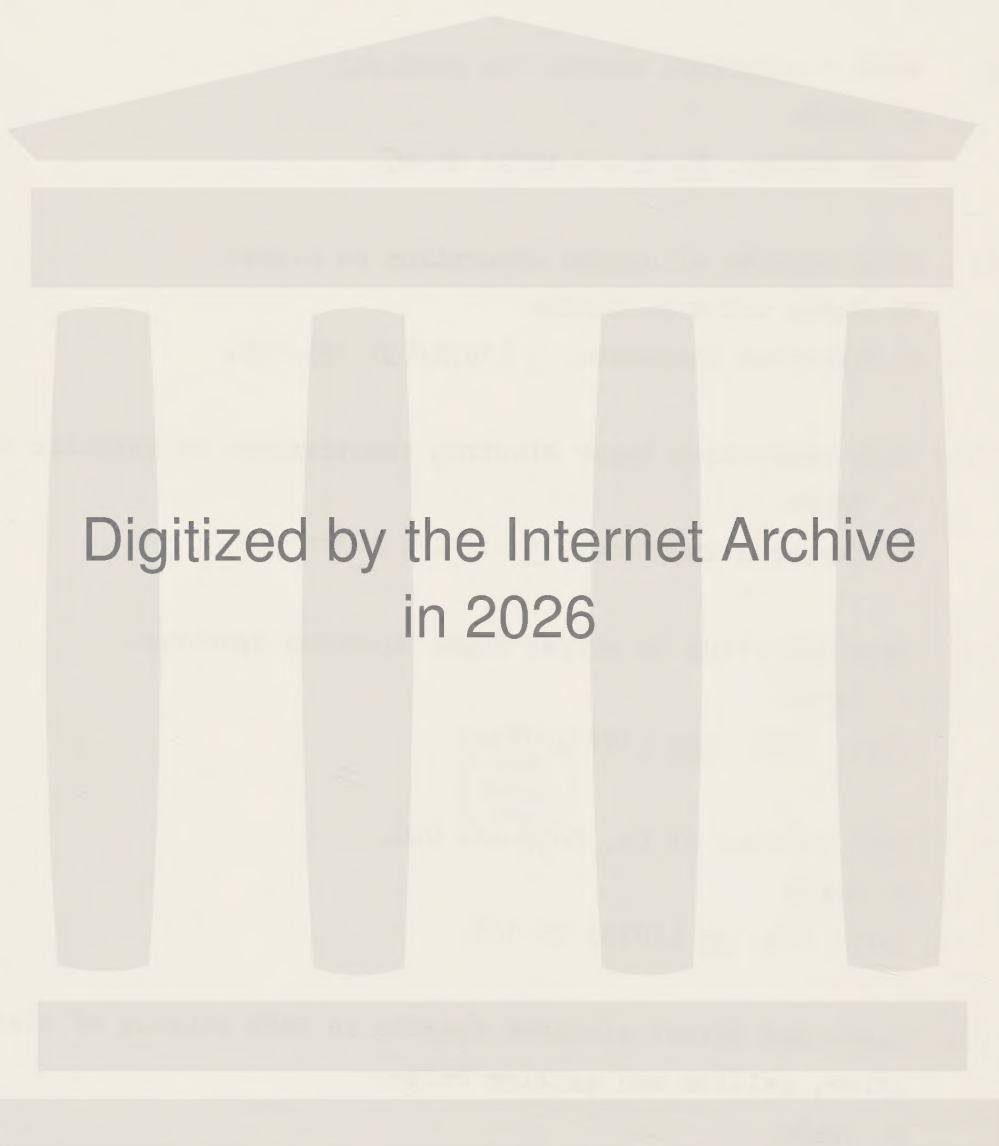
ESCA STUDIES OF METALS AND OXIDES

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The thesis consists of this summary and the following papers.

- I. ESCA - a surface method (in Swedish).
G. Schön
Kem. Tidskr. 84 Nr 6 (1972) 40-46.
- II. ESCA studies of oxygen adsorption on nickel.
G. Schön and S.T. Lundin
J. Electron Spectrosc. 1 (1972/73) 105-109.
- III. High resolution Auger electron spectroscopy of metallic copper.
G. Schön
J. Electron Spectrosc. 1 (1972/73) 377-387.
- IV. Spin splitting in copper Auger electron spectrum.
G. Schön
Phys. Lett. 42A (1973) 381-2.
- V. ESCA studies of Cu, Cu₂O and CuO.
G. Schön
Surf. Sci. 35 (1973) 96-108.
- VI. Auger and direct electron spectra in ESCA studies of zinc, zinc oxide, gallium and gallium oxide.
G. Schön
J. Electron Spectrosc. 2 (1973). In press.
- VII. ESCA studies of Ag, Ag₂O and AgO.
G. Schön
Acta Chem. Scand. In press.

In the following text these works are referred to as I - VII.



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INTRODUCTION

Electron spectroscopy is based upon energy analysis at high resolution of the electrons which are emitted from a substance on irradiation. The sample can be irradiated in different ways. When photons are used, a distinction is normally made between high-energy photons (x-rays) and low-energy photons (ultra violet light). The former method is often called x-ray photoelectron spectroscopy (XPS) and the latter ultra violet photoelectron spectroscopy (UPS). In UPS only the valence electrons can be excited. This is why the method is also called molecular photoelectron spectroscopy. The study of gaseous molecules with UPS was mainly developed by D.W. Turner and coworkers at Oxford¹.

The use of x-rays as a source of excitation energy was developed in Uppsala by K. Siegbahn and coworkers^{2,3}. They named the method ESCA (Electron Spectroscopy for Chemical Analysis). Not only directly excited photoelectrons but also Auger electrons are studied. The description XPS is thus not very informative, since Auger electrons are excluded. Thus the original designation ESCA is preferred in this work. In the literature the term IEE (Induced Electron Emission) can also be found.

In the work described in this thesis only x-ray irradiation has been used. Photoelectrons are emitted according to the photoelectric law:

$$E_{\text{kin}} = h\nu - E_{\text{bind}}$$

where E_{bind} = electron binding energy

E_{kin} = kinetic energy of emitted electron

$h\nu$ = x-ray energy

Thus electron binding energies can be measured and the substance under investigation can be analysed with respect to occurring elements. However, such an analysis can also be performed with x-ray spectroscopy. The ESCA method has two characteristics which make it a very powerful analytical tool;

1. The electron binding energy depends on the chemical environment. Shifts of several eV can be found between chemically non-equivalent atoms.
2. Only a thin surface layer is analysed, since the escape depth of ejected electrons is small, 10-20 Å.

The chemical shifts due to different chemical environments and the surface sensitivity are the two most important properties of ESCA. However, several other phenomena also appear which, interpreted correctly, increase information about the substance under investigation.

Such a phenomenon is spin splitting, also called multiplet or exchange splitting, which appears in paramagnetic compounds. If an atom has unpaired electrons in its ground state the binding energy is different for spin-up and spin-down electrons.

Satellite signals are also present due to shake-up processes, which means that one electron in the valence band is excited to an unoccupied state parallel with the formation of a core electron vacancy.

When an electron penetrates the substance, it may lose energy in discrete amounts due to plasmon losses. A plasmon is a quantized collective excitation of an electron gas. The plasmon energy, 10-20 eV, is characteristic of the substance under investigation.

The signal width is primarily due to the life-time of the vacancy according to the uncertainty relation

$$\Delta E \cdot \Delta t \geq \hbar$$

The vacancy life-time is not constant for a particular electron level but depends on the chemical environment.

As mentioned above, not only photoelectrons but also Auger electrons are analysed. Most attention has hitherto been paid to photoelectrons in ESCA studies, since signals from these are not so complex as these from Auger signals. In this thesis, metals and metal oxides have been studied with respect to both photoelectrons and Auger electrons, and it will be shown that Auger electron signals may give more information than the photoelectron signals.

The electron spectroscopy literature is growing very fast at the present time. Commercial instruments have been available since 1970, which has accelerated the development. A vast amount of ESCA information is collected in the two monographs by the Uppsala group^{2,3}. The proceedings of an international conference in 1971⁴ also cover all aspects of electron

spectroscopy. Recently a small book appeared⁵, which could serve as a brief introduction to the field.

EXPERIMENTAL

The measurements have been performed with an AEI ES 100 electron spectrometer. Figure 1 shows the instrument schematically. The x-ray generator was normally operated at 15 kV and 20 mA (300 W). All results presented in this thesis were obtained with an aluminium anode, which gives an $\text{AlK}\alpha_{1,2}$ radiation of 1486.6 eV. During the calibration (paper III) a magnesium anode was also used, which gives a $\text{MgK}\alpha_{1,2}$ radiation of 1256.6 eV. A thin aluminium window, positioned between the anode and the sample, filters the x-rays and prevents the electrons from the filament reaching the analyser. The sample can be heated to 400°C and cooled to liquid nitrogen temperature (-196°C). In this work the heating facilities were frequently used.

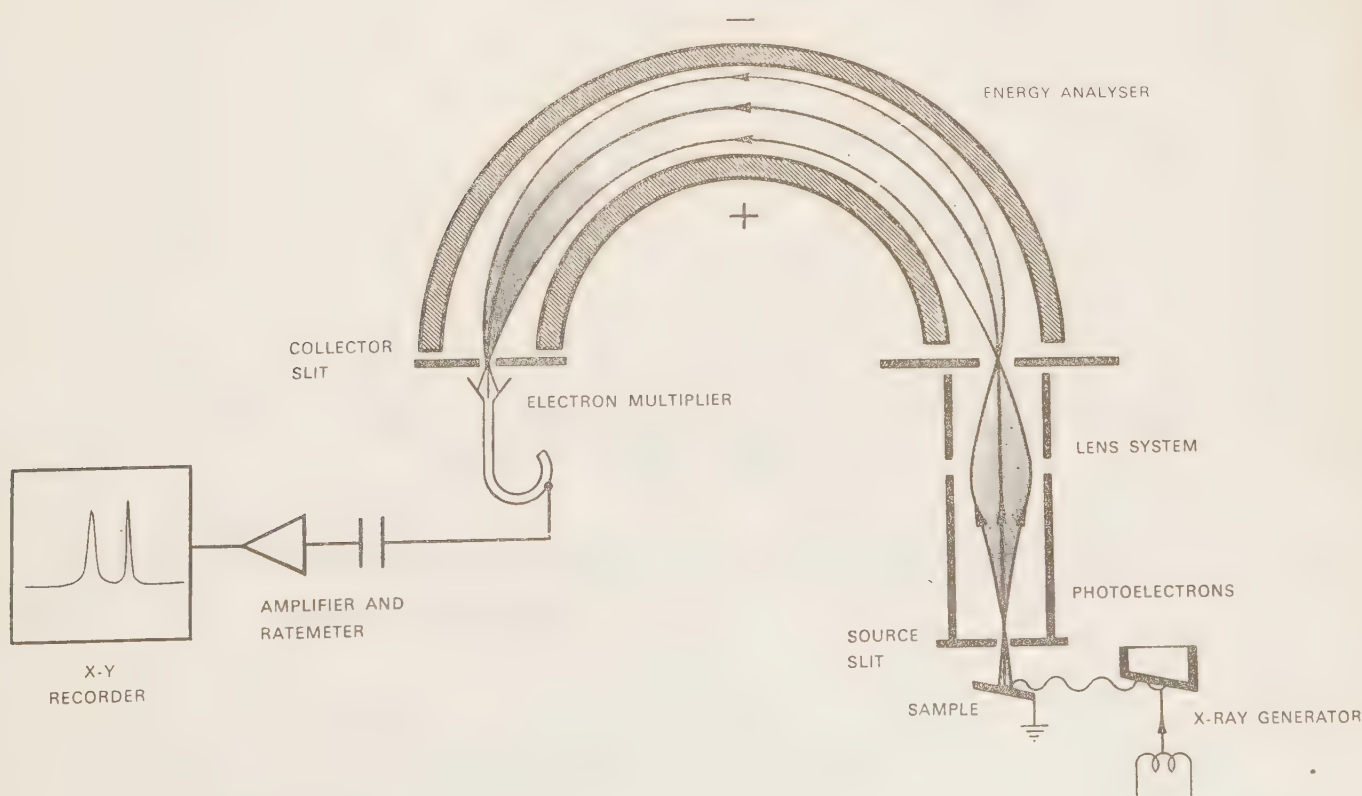


Figure 1. Basic arrangement of an electron spectrometer. (AEI ES 100).

The instrument is equipped with a double-focusing hemispherical electrostatic analyser enclosed within the vacuum system by a μ -metal screen. In the lens system the electrons are preretarded. The collector slit width can be varied while the instrument is operating. Figure 2 shows Ag 3d electron spectra from a metallic silver foil recorded with three different collector slits. Distinct differences in FWHM (full width at half maximum) and intensities are found. When the magnesium anode was used instead of the aluminium one, a FWHM of 0.85 eV was obtained with the narrowest slit. The narrower signal width with MgK α radiation compared to AlK α radiation is due to a smaller energy spread of the magnesium radiation. With a Hewlett-Packard ESCA instrument equipped with an x-ray monochromator, an Au 4f $_{7/2}$ electron signal with a FWHM of 0.7 eV was recorded⁶.

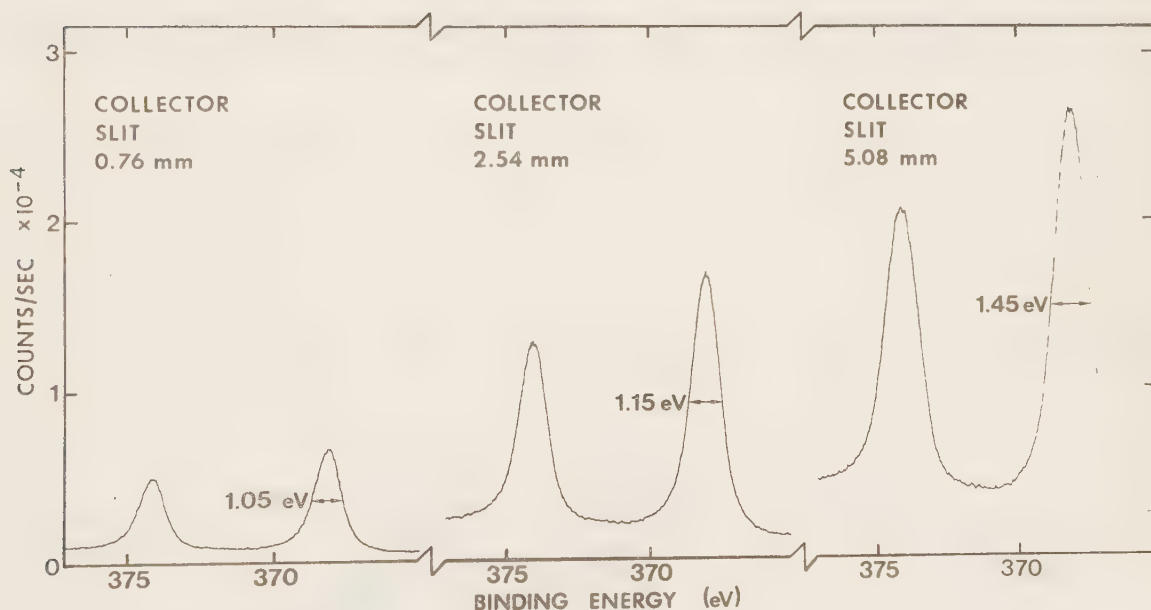


Figure 2. Ag 3d electron spectra from metallic silver at 400°C.
AlK $\alpha_{1,2}$ -radiation.

Since non-monochromatic radiation has been used in this work more than one x-ray energy is present in the aluminium radiation. In Figures 3 and 4 Ag 3d electron signals from different Al x-rays are shown. The main peaks are due to AlK $\alpha_{1,2}$ and are so close together that only one signal

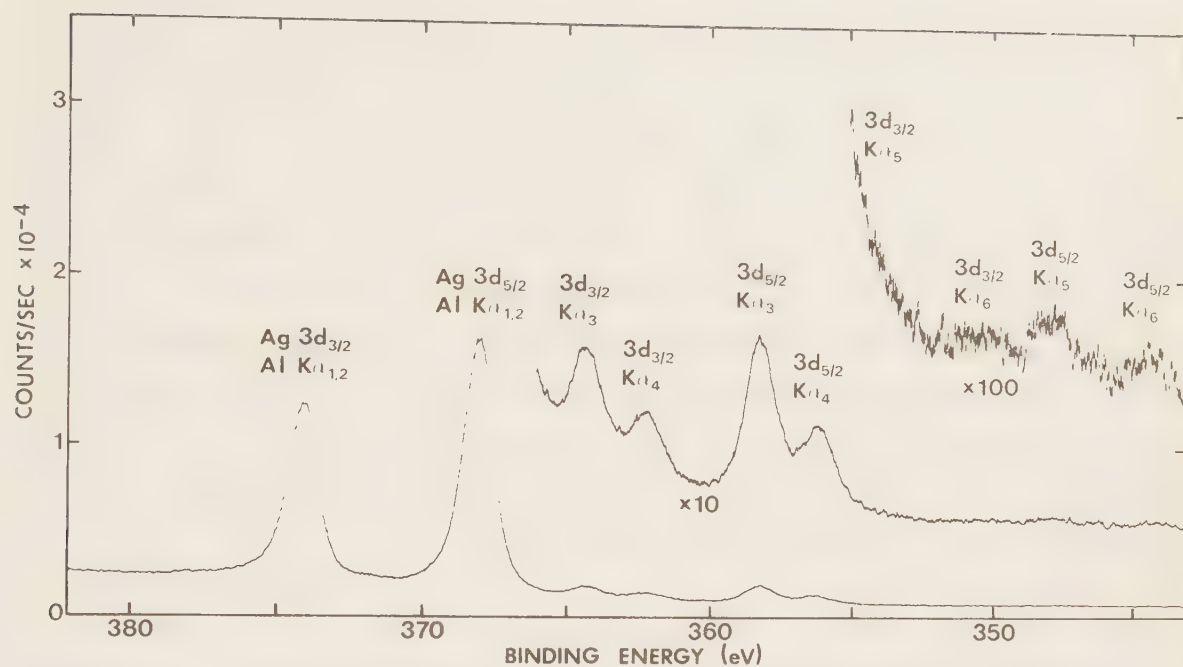


Figure 3. Ag 3d electron spectra from metallic silver at 400°C. AlK α -radiation.

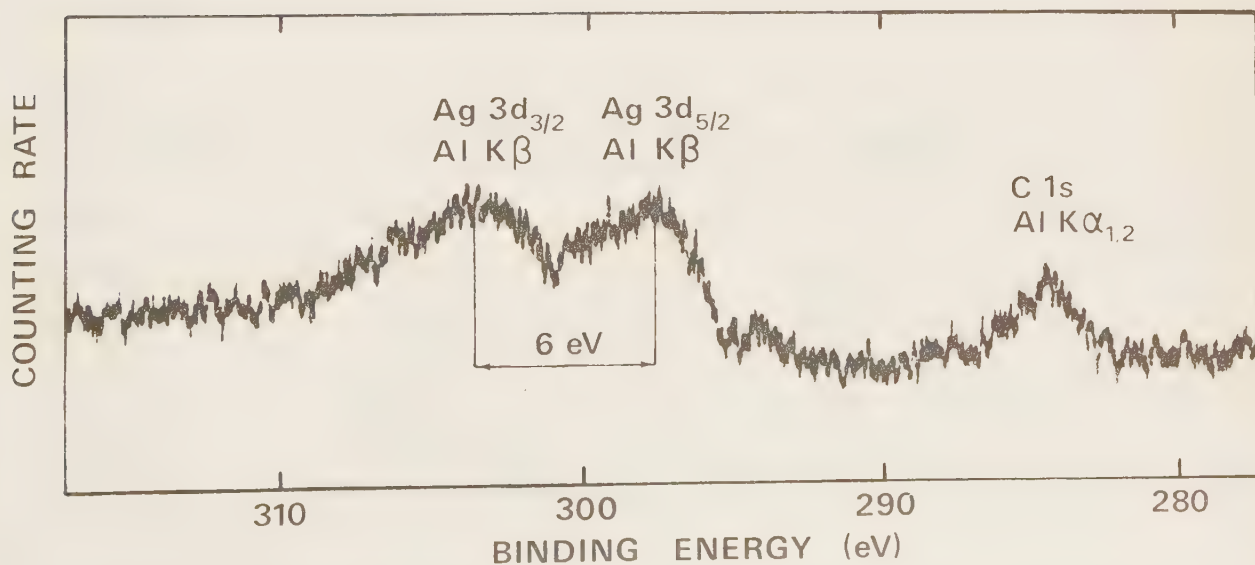


Figure 4. Electron spectrum from metallic silver at 400°C. Al-radiation.

is recorded for each electron level. $\text{AlK}\alpha_{3,4}$, $\text{AlK}\alpha_{5,6}$ and $\text{AlK}\beta$ signals are also found. $\text{AlK}\beta$ radiation is present due to a transition from the aluminium valence band to the $1s$ vacancy. In this example the $\text{Ag } 3d$ signals from $\text{AlK}\beta$ radiation have about the same intensity as the $\text{C } 1s$ signal. Thus, the $\text{AlK}\beta$ signals can be interpreted as normal photoelectrons arising from the $\text{AlK}\alpha_{1,2}$ radiation. It should be pointed out that $\text{AlK}\beta$ signals appear at 70.3 eV higher kinetic energy than the $\text{AlK}\alpha_{1,2}$ signals. $\text{AlK}\alpha_{3,4}$ and $\text{AlK}\alpha_{5,6}$ x-rays are satellites due to multiple ionization of the aluminium atoms. $\text{K}\alpha_{3,4}$ satellites appear due to a vacancy in both $1s$ and $2p$ levels while $\text{K}\alpha_{5,6}$ satellites are associated with one vacancy in the $1s$ level and two vacancies in the $2p$ level³. Table 1 summarizes the Al x-rays energies as measured in this work with an $\text{AlK}\alpha_{1,2}$ reference energy of 1486.6 eV⁷. The peak heights have been used in the determination of relative intensities.

In Figure 5 the AEI ES 100 vacuum system is shown. Two oil diffusion pumps for sample chamber and analyser, equipped with thermoelectric baffles and liquid nitrogen cold traps, produce a vacuum of $10^{-6} - 10^{-7}$ torr during the measurements. The sample is introduced through one of the insertion locks.

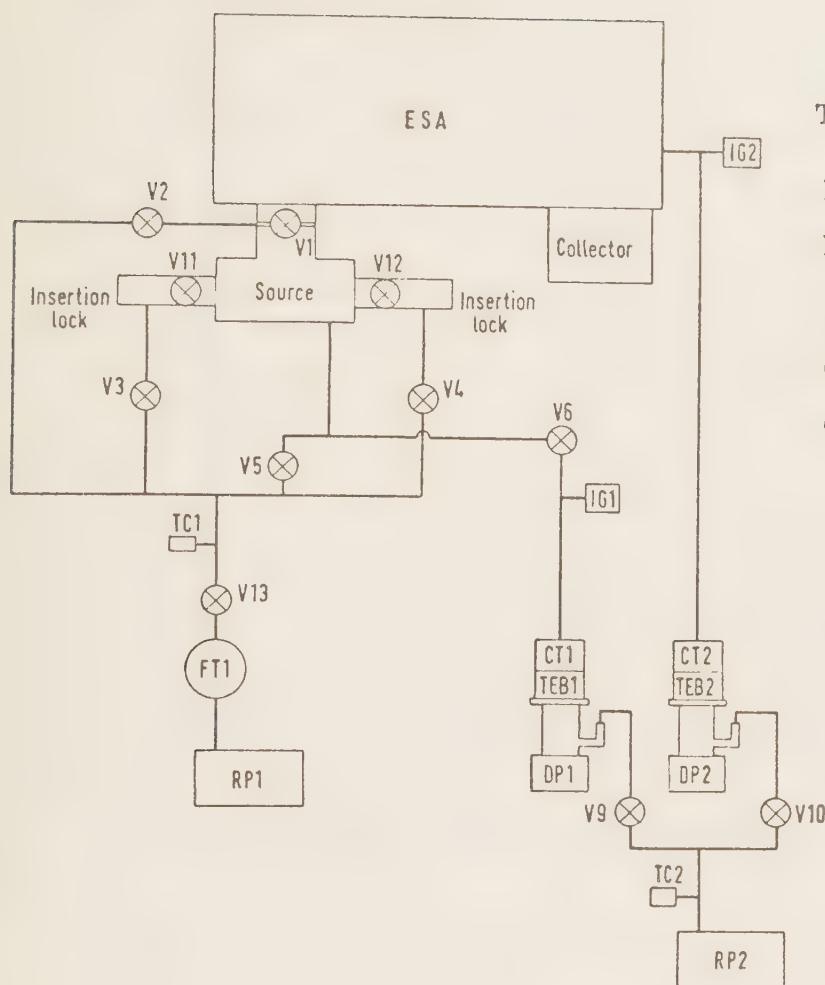
TABLE 1

Aluminium x-ray energies

Designation	Energy, eV	Relative intensity
Al $\text{K}\alpha_{1,2}$	1486.6	1
Al $\text{K}\alpha_3$	1496.4	0.06
Al $\text{K}\alpha_4$	1498.4	0.03
Al $\text{K}\alpha_5$	1506.8	0.002
Al $\text{K}\alpha_6$	1510.2	0.001
Al $\text{K}\beta$	1556.9	0.005

In Figure 5 the AEI ES 100 vacuum system is shown. Two oil diffusion pumps for sample chamber and analyser, equipped with thermoelectric baffles and liquid nitrogen cold traps, produce a vacuum of $10^{-6} - 10^{-7}$ torr during the measurements. The sample is introduced through one of the insertion locks.

Vacuum System



Typical operating pressures (torr):

IG1 - Better than 5×10^{-5}

IG2 - X-ray tube limit better than 10^{-5} .
Surface contamination may set better pressure requirement.

TC1 - Better than 0.05

TC2 - Better than 0.05

KEY

CT - Cold trap

DP - Diffusion pump

FT - Foreline trap

IG - Ionization gauge

RP - Rotary pump

TC - Thermocouple gauge

TEB - Thermoelectric baffle

V - Valve

Figure 5. AEI ES 100 vacuum system.

During part of the work an AEI QMS 40 quadrupole mass spectrometer was attached to the sample chamber. Figure 6a shows a residual mass spectrum after the vacuum system was baked out. The main peaks belong to H_2 (mass number 2) and water (mass number 18). When the x-ray unit is switched on, the pressure increases and the resulting mass spectrum is shown in Figure 6b. Now the spectrum is also dominated by CO (mass number 28) and CO_2 (mass number 44). Around mass number 28, peaks appear due to C_2 fractions ($25 = C_2H^+$, $26 = C_2H_2^+$, $27 = C_2H_3^+$ a.s.o.) C_1 fractions are also present.

The energy calibration is described in detail in paper III.

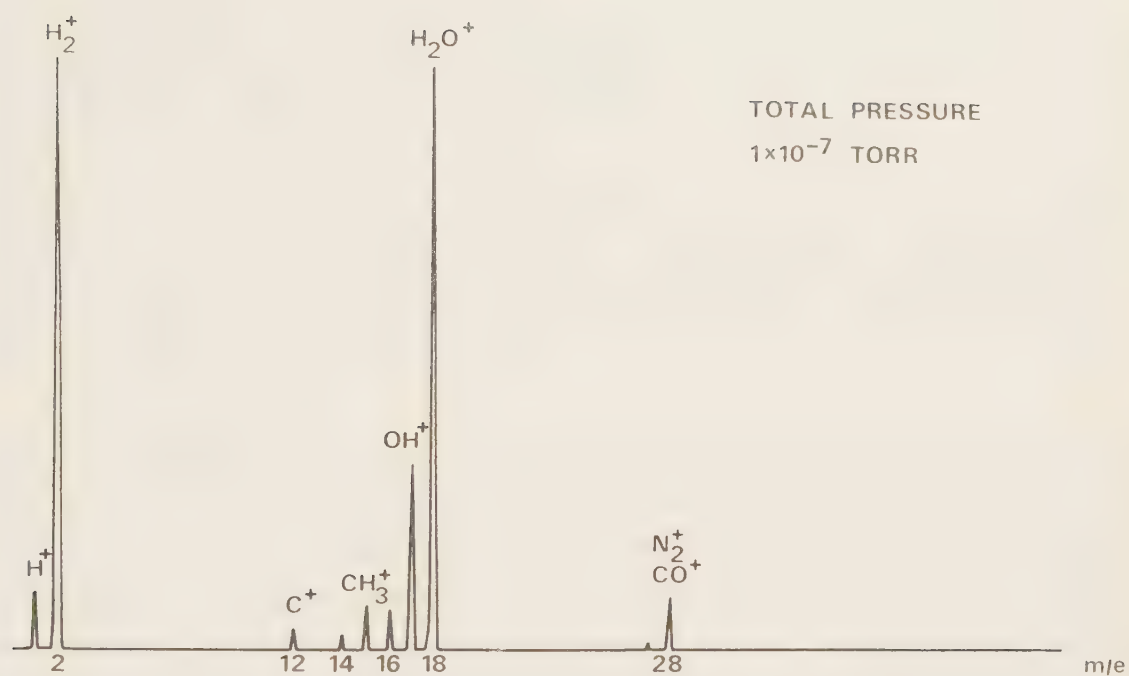


Figure 6a. Residual mass spectrum from sample chamber after baking.

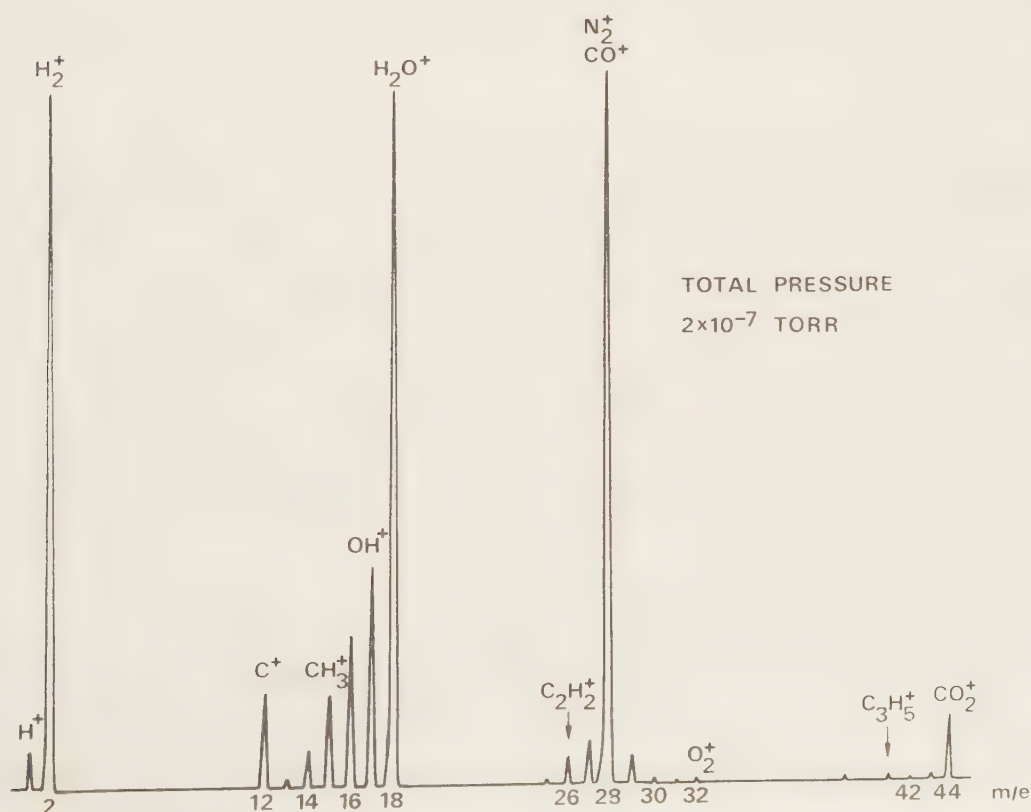


Figure 6b. Residual mass spectrum from sample chamber during operation.

SUMMARY OF PAPERS I - VII

Paper I (in Swedish) gives an introduction to ESCA as a surface method. Experimental results from the literature (also from papers II and III) illustrate the surface sensitivity of ESCA.

It has been predicted that electron spectroscopy will be a very powerful method for the study of solid catalysts. Many catalytic mechanisms are unknown, partly due to lack of information about the true nature of the catalyst surface.

We have previously studied the oxidation of ethylene to ethylene oxide over a silver-containing catalyst⁸. The catalysts were prepared and tested with respect to activity and selectivity. Part of the ethylene is oxidized to carbon dioxide and water. By adding BaO_2 and NaCl during the preparation of the catalyst a maximum selectivity of 80 % was attained. This means that 80 % of the reacted ethylene was converted to the desired product, ethylene oxide.

The nature of the silver catalyst surface phase has not yet been established. Usually it is called a silver catalyst, but sometimes the designation silver oxide catalyst is used. The existence of surface oxides has been reported.

Vol and Shishakov⁹ found, by electron diffraction, AgO_2 on the surface of an evaporated silver film exposed to oxygen at close to atmospheric pressure at 100-150°C. Kagawa *et al.*¹⁰ found AgO_2 and Ag_2O on both a silver catalyst used for ethylene oxidation and on silver exposed to oxygen. The techniques used for surface characterization were electron diffraction and IR absorption. Feller-Kniepmeier *et al.*¹¹ have shown by a combination of x-ray and electron diffraction, that a layer of Ag_2O_3 exists on technical silver catalysts which have been used at a reactor temperature of 200-300°C.

In order to contribute to the characterization of the catalyst surface phase, silver catalysts⁸ were studied by ESCA. In active form the silver was supported on $\alpha\text{-Al}_2\text{O}_3$. Before investigation by ESCA the silver phase was separated from the carrier by sifting, and the separated powder was placed on a copper gauze.

In paper I, oxygen 1s electron spectra from metallic silver foil, silver catalyst, Ag_2O and AgO are reported. The oxygen signals from the metallic silver foil and the silver catalyst are very similar, whereas the silver oxides show two characteristic oxygen peaks. From the results it is concluded that there is no indication that the catalyst surface layer consists of Ag_2O or AgO . The catalyst surface phase is probably metallic silver.

However, it must be emphasized that the catalyst surface during operating conditions can be different from that during the ESCA examination at room temperature and low pressure.

In paper II, a metallic nickel foil was studied. At room temperature the Ni 2p spectrum was characteristic of a mixture of nickel oxide and metallic nickel. Thus the surface was oxidized as is usual for most metal surfaces in atmospheric environment. Two oxygen peaks were present. After the temperature had been raised to 300°C the oxygen signal decreased and there was no oxide structure in the Ni 2p electron spectrum. After exposure to atmosphere at room temperature the high-binding energy oxygen signal appeared. This peak was interpreted as due to adsorbed oxygen. The same interpretation has recently been suggested by Robert *et al.*¹². It is also possible that it is due to absorbed oxygen in the surface region of nickel. A complex satellite structure was also built up adjacent to the metallic nickel peaks. The result clearly shows the usefulness of ESCA in adsorption studies.

In ESCA studies most attention has been paid to directly excited photoelectrons, but also Auger electrons find their way to the analyser. A large part of this thesis is devoted to a comparison between directly excited photoelectron signals and Auger electron signals.

The results of studies on the copper - copper oxide system are presented in paper III, IV and V. In paper III the electron binding energies for metallic copper and the copper LMM Auger electron spectrum are reported. Fine structure not earlier observed was found in the Auger spectrum. Recently, other high resolution Auger electron spectroscopy studies of Cu have been published^{13,14}, the results of which agree with those presented here. Most interesting in paper III is the difference in sensitivity for surface oxygen between the photoelectron and Auger electron

signals. The Cu $L_3M_{4,5}M_{4,5}$ Auger signal is changed very distinctly upon heating, when oxygen disappears from the surface region. On the contrary, the Cu 2p electron lines do not change at all upon this treatment. This indicates, for the first time, that Auger signals may be more sensitive to the chemical environment than the directly excited photoelectron signals. The main $L_3M_{4,5}M_{4,5}$ Cu Auger peak is very narrow, although the copper valence band is doubly involved in the transition. This result contradicts the opinion that when the valence band is involved in the Auger transition broad Auger signals are obtained. The result presented here indicates different transition probabilities in different parts of the valence band.

In paper IV, a detailed study of the Cu $L_3M_{1,2,3}$ signal from metallic Cu is reported. Two peaks with the intensity ratio 3:1 are found, indicating a triplet-singlet splitting. This is an experimental verification of spin splitting in Auger spectra.

In paper V, the copper investigation is extended to the oxides. Cu 2p, Cu 3d and O 1s electron spectra and Cu $L_3M_{4,5}M_{4,5}$ Auger electron spectra from Cu, Cu₂O and CuO are studied at 25°C and at 400°C. The Auger signal is more sensitive to the chemical environment than the photoelectron signals. The Auger shift is about 2 eV between metallic and oxide copper. The Cu 2p electron shift is not so pronounced. Satellite peaks accompanying the Cu 2p electron lines are also studied.

Paper VI gives the results from a study of zinc - zinc oxide and gallium - gallium oxide. Electron binding energies are given for both metal and oxide states. The chemical shift between zinc electron binding energies is very small, whereas the zinc Auger electron signals are separated by 4.3 eV. This separation appears both for $L_{2,3}M_{4,5}M_{4,5}$ and $L_{2,3}M_{2,3}M_{4,5}$ Auger signals. In gallium, the oxide and metal signals are separated by 1.9 eV, but the Auger electron energy shift is three times as large. Thus it is shown again that the Auger signals can be more sensitive to the chemical environment than the direct electron signals. Paper VI also discusses the line widths of the Auger signals. As for metallic copper, the $L_3M_{4,5}M_{4,5}$ main peaks are narrower than the widths of the involved electron levels.

The surface sensitivity of ESCA is also shown in paper VI, where metallic gallium covered with a surface oxide was studied. Photoelectrons with high kinetic energy (Ga 3d electrons) have a larger contribution from the metal

than photoelectrons with a low kinetic energy ($\text{Ga } 2p_{3/2}$), since the electron escape depth increases with the kinetic energy.

In paper VII, a detailed investigation of Ag, Ag_2O and AgO is reported. For metallic silver, electron binding energies from the $3s$ level and levels above this are given. The three compounds are compared with respect to Ag $3d$ binding energy, O $1s$ binding energy, valence band structure and MNN Auger spectrum. Ag $3d$ binding energies decrease in the order Ag, Ag_2O and AgO, which is in an opposite direction compared to all other metal - metal oxide systems reported in the literature. The chemical shift between Ag and Ag_2O is 0.4 eV and between Ag and AgO 0.7 eV. An Ag $3d_{5/2} 4d_{5/2}$ Auger electron energy shift of 0.7 eV exists between silver in the metallic and the oxide state. In metallic Ag the $3d_{5/2} 4d_{5/2}$ Auger signal is split into at least three components. The oxygen signal is the most characteristic feature of a particular compound; Ag has one O $1s$ peak at a binding energy of 532.2 eV, Ag_2O two peaks at 529.0 and 530.4 eV and AgO two peaks at 528.4 and 530.3 eV. The thermal decomposition of Ag_2O and AgO was also studied.

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Gunnar Schön

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